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ELECTROLYTIC SOLUTION FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY USING SAME

[Richiumu niji denchi yo denkaieki oyobi sore wo mochiita richiumu niji denchi]

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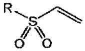
[Claim(s)] /2*

[Claim 1] An electrolytic solution in which an electrolyte is dissolved in a nonaqueous solvent; said electrolytic solution for a lithium secondary battery characterized by a vinyl sulfone derivative represented by the following general formula (I):

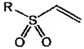
[Formula 1]



(where R denotes an alkyl group having 1 to 12 carbons, an alkenyl group having 1 to 12 carbons, and a cycloalkyl group having 3 to 6 carbons) being contained in said electrolytic solution.

[Claim 2] A lithium secondary battery comprising a positive electrode, negative electrode and an electrolytic solution wherein an electrolyte is dissolved in a nonaqueous solvent; said lithium secondary battery characterized by a vinyl sulfone derivative represented by the following general formula (I):

[Formula 2]



(where R denotes an alkyl group having 1 to 12 carbons, an alkenyl group having 1 to 12 carbons, and a cycloalkyl group having 3 to 6 carbons) being contained in said electrolytic solution.

[Detailed Explanation of the Invention]

* Claim and paragraph numbers correspond to those in the foreign text.

[0001]

[Industrial Field of the Invention] The present invention relates to a novel electrolytic solution for a lithium secondary battery wherein a secondary battery having outstanding battery characteristics, such as cycle characteristics, electrical capacity, and storage characteristics, of a battery can be provided, and a lithium secondary battery employing it.

[0002]

[Prior Art] Lithium secondary batteries have been used widely in recent years as power supplies for small electronic equipment. A lithium secondary battery is composed mainly of a positive electrode, a nonaqueous electrolytic solution and a negative electrode. In particular, a lithium secondary battery, in which a lithium compound oxide, such as $LiCoO_2$, is used as the positive electrode and a carbon material or lithium metal is used as the negative electrode, is used ideally. A carbonate, such as ethylene carbonate (EC) or propylene carbonate (PC), is used ideally for the electrolytic solution for a lithium secondary battery thereof.

[0003]

[Problems to be Solved by the Invention] However, the battery characteristics, such as the battery cycle properties and electrical capacitance, of a secondary battery having more outstanding characteristics is demanded. Peeling of the carbon material of a lithium secondary battery employing a highly crystallized carbon

material, such as a natural graphite or artificial graphite, as the negative electrode is observed, and the capacity may be irreversible due to this peeling phenomenon, which occurs because the solvent in the electrolytic solution dissolves the carbon material at the time of charging, which is thus attributed to an electrochemical reduction of the solvent in the interface between carbon material and the electrolytic solution. Of the carbon materials, a PC having a low melting point and a high-permittivity also has a high electrical conductance at low temperature. But when a graphite negative pole was employed, there was a problem because decomposition of the PC occurred, and it could not be used for a lithium secondary battery. Partial decomposition of the EC occurred during repeated charging and discharging, and a reduction in the battery performance resulted. Thus, the status quo is that the battery characteristics, such as the battery cycle properties and electrical capacitance, were not always satisfactory.

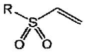
[0004] It is an object in solving the problems related to an electrolytic solution for a lithium secondary battery, as mentioned above, to provide an electrolytic solution for a lithium secondary battery having the outstanding battery cycle characteristics, and further, having excellent battery characteristics, such as electrical capacity and storage characteristics in a charged state, and a lithium secondary battery using it.

[0005]

[Means for Solving the Problems] The present invention relates to an electrolytic solution in which an electrolyte is dissolved in a nonaqueous solvent; said electrolytic solution for a lithium secondary battery characterized by a vinyl sulfone derivative represented by the following general formula (I):

[0006]

[Formula 3]

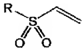


[0007] (where R denotes an alkyl group having 1 to 12 carbons, an alkenyl group having 1 to 12 carbons, and a cycloalkyl group having 3 to 6 carbons) being contained in said electrolytic solution.

[0008] The present invention relates to a lithium secondary battery comprising a positive electrode, negative electrode and an electrolytic solution wherein an electrolyte is dissolved in a nonaqueous solvent; said lithium secondary battery characterized by a vinyl sulfone derivative represented by the following general formula (I):

[0009]

[Formula 4]



[0010] (where R denotes an alkyl group having 1 to 12 carbons, an alkenyl group having 1 to 12 carbons, and a cycloalkyl group having 3 to 6 carbons) being contained in said electrolytic solution.

[0011] The aforesaid vinyl sulfone derivative contained in the electrolytic solution is considered to contribute to the formation of a passivation coating on the surface of the carbon material. A highly crystallized carbon material that is activated by natural graphite, artificial graphite, and the like, is covered with the passivation coating to have an effect for suppressing the decomposition of the electrolytic solution without impairing the normal reactions of the battery.

[0012]

[Embodiments of the Invention] R of the vinyl sulfone derivative represented by the aforesaid formula (I) in the compound contained in the electrolytic solution wherein an electrolyte is dissolved in a nonaqueous solvent is preferably an alkyl group, such as a methyl group, ethyl group or propyl group, having 1 to 12 carbons. The alkyl group may be a branched alkyl group, such as an isopropyl group or an isobutyl group. In addition, it may be an alkenyl group, such as a vinyl group or allyl group; and a cycloalkyl group having 3 to 6 carbons, such as a cyclopropyl group of cyclohexyl group.

[0013] Divinyl sulfone (R=vinyl group), ethylvinyl sulfone (R=ethyl group), isopropylvinyl sulfone (R=isopropyl group), cyclohexylvinyl sulfone (R=cyclohexyl group), and the like are cited

as specific examples of the vinyl sulfone derivative represented by the aforesaid Formula (I).

[0014] When the aforesaid sulfone derivative is added, if the content of the vinyl sulfone derivative represented by the aforesaid Formula (I) is excessively high, the conductivity of the electrolytic solution and the like vary and the battery performance may diminish. In addition, if it is excessively low, a sufficient coating is not formed and the anticipated battery performance is not obtained; hence, a range of 0.01 to 20% by weight, and in particular, 0.1 to 10% by weight with respect to the weight of the electrolytic solution is preferable.

[0015] It is preferable that the nonaqueous solvent used in the present invention comprise a high-permittivity solvent and low-viscosity solvent. Cyclic carbonates, such as ethylene carbonate (EC), propylene carbonate (PC) and butylene carbonate (BC), are cited ideally as examples of high-permittivity solvents. These high-permittivity solvents may be used singly or they may be used by combining at least two of them.

[0016] Chain carbonates, such as dimethyl carbonate (DMC), methylethyl carbonate (MEC) and diethyl carbonate (DEC); ethers, such as tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane and 1,2-dibutoxyethane; lactones, such as γ-butyrolactone; nitriles, such as acetonitrile; esters, such as methyl propionate; and amides, such as dimethyl formamide, are

cited as examples of the low-viscosity solvent. These low-viscosity solvents may be used singly, or they may be used by combining two or more of them. The high-permittivity and low-viscosity solvents are used respectively by selecting and combining them arbitrarily. Moreover, the aforesaid high-permittivity and low-viscosity solvents are used at a ratio by volume (high-permittivity solvent: low-viscosity solvent) that is normally 1:9 to 4:1, and preferably, 1:4 to 7:3.

[0017] $LiPF_6$ $LiBF_4$, $LiClO_4$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiC(SO_2CF_3)_3$, and the like are cited as examples of electrolytes used in the present invention. These electrolytes may be used singly or they may be used by combining two or more of them. These electrolytes may be used normally by being dissolved at a concentration of 0.1 to 3 M, and preferably, 0.5 to 1.5 M.

[0018] The electrolytic solution of the present invention is obtained by, e.g., mixing the aforesaid high-permittivity solvent and the low-viscosity solvent, dissolving the aforesaid electrolytic solution therein, and dissolving the vinyl sulfone derivative, represented by the aforesaid Formula (I).

[0019] The electrolytic solution of the present invention is used ideally as a component of a secondary battery, and in particular, a lithium secondary battery. The components besides the electrolytic solution composing the secondary battery are not limited in

particular, and various components that are used conventionally may be used.

[0020] A compound metal oxide of lithium and at least one kind of metal selected from a group comprising cobalt, manganese, nickel, chromium, iron and vanadium are used for the positive electrode material (positive electrode active material). $LiCoO_2$、$LiMn_2O_4$、$LiNiO_2$, and the like are cited as examples of such a compound metal oxide.

[0021] The positive electrode was manufactured by kneading the aforesaid positive electrode material with a conductive agent, such as acetylene black or carbon black, and a binder, such as polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF), to obtain a positive electrode mixture, after which it was rolled into an aluminum stainless steel foil or las board [as transliterated], and heat treating it at a temperature of about 50 to 250°C for about 2 hours under a vacuum.

[0022] Substances, such as carbon materials having metallic lithium, a lithium alloy, a graphite-type crystal structure which can occlude and release lithium (pyrolytic carbon, coke, graphite (artificial graphite, natural graphite, etc.), an organic polymer compound combusted matter, carbon fibers) and a compound tin oxide, are used for the negative electrode (negative active material). In particular, it is preferable to use a carbon material having a graphite-type crystal structure wherein the layer distance (d_{002}) of the lattice plane (002) is 3.35 to 3.40Å. Moreover, a powder material,

such as a powder carbon material, is used as the negative mixture by kneading it with a binder, such as ethylene propylene diene terpolymer (EPDM), polytetrafluoroethylene (PTFE) or polyvinylidene fluoride (PVDF).

[0023] The structure of the lithium secondary battery is not limited in particular, and a coin battery having a positive electrode, negative electrode and single-layer or multilayer separator, and further, a cylindrical battery or a prismatic battery having a positive electrode, negative electrode and separator roll, and the like are cited as examples therefor. Moreover, a fine porous film, woven fabric, nonwoven fabric, and the like made of a known polyolefin are used for the separator.

[0024]

[Practical Examples] Although the present invention is described specifically next by citing practical examples and comparative examples, these examples are not intended to restrict the present invention at all.

Practical Example 1

(Preparation of the electrolytic solution) A nonaqueous solvent having a PC:DMC (ratio by volume) of 1:2 was prepared, $LiPF_6$ was so dissolved therein to a concentration of 1 M, after which divinyl sulfone (R=vinyl group) was so further added, as an additive, to the electrolytic solution to 2.0% by weight.

[0025] (Manufacture of lithium secondary battery and measurement of battery characteristics) 80% by weight of $LiCoO_2$ (positive electrode active material), 10% by weight of acetylene black (conductive agent) and 10% by weight of polyvinylidene fluoride (binder) were mixed, N-methyl pyrrolidone was added thereto to obtain a slurry, and then coated an aluminum foil. This was subsequently dried and subjected to an isostatic pressing to prepare the positive electrode. 90% by weight of a natural graphite (negative electrode active material) and 10% by weight of polyvinylidene fluoride (binder) were mixed, N-methyl pyrrolidone was added thereto to obtain a slurry, and then coated on copper foil. This was subsequently dried and subjected to isostatic pressing to prepare the negative electrode. A coin battery (diameter: 20 mm; thickness: 3.2 mm) was manufactured by using a separator made of a polypropylene fine porous film and injecting the above-mentioned electrolytic solution. This coin battery was used to perform a 5-hour charging to a termination voltage of 4.2 V at a constant current of 0.8 mA and constant voltage under room temperature (20°C), perform discharging to a termination voltage of 2.7 V under a constant current of 0.8 mA next, and this charging and discharging were repeated. The initial charge/discharge capacity was nearly equivalent to a case in which EC-DMC (1/2) was employed as the electrolytic solution (Comparative Example 2), and upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 86.1% when the initial

discharge capacity was 100%. In addition, the low-temperature characteristics also were satisfactory. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0026] Practical Example 2

Other than using 0.5% by weight, with respect to the electrolytic solution, of divinyl sulfone (R=vinyl group), the electrolytic solution was prepared and the coin battery was manufactured as in Practical Example 1, and upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 84.7%. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0027] Practical Example 3

Other than using 8.0% by weight, with respect to the electrolytic solution, of divinyl sulfone (R=vinyl group), the electrolytic solution was prepared and the coin battery was manufactured as in Practical Example 1, and upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 81.1%. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0028] Practical Example 4

Other than using 2.0% by weight, with respect to the electrolytic solution, of ethylvinyl sulfone (R=vinyl group), the electrolytic solution was prepared and the coin battery was manufactured as in

Practical Example 1. Upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 85.7%. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0029] Comparative Example 1

A nonaqueous solvent having a PC:DMC (ratio by volume) of 1:2 was prepared and $LiPF_6$ was so dissolved therein to a concentration of 1 M. No additive was added at all at this time. Upon manufacturing a coin battery as in Practical Example 1 by using this electrolytic solution and measuring the battery characteristics, decomposition of the PC occurred during the first charge and the battery could not be discharged at all. As a result of dismantling the battery after the first charge and observing it, peeling of the graphite negative electrode was recognized. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

[0030] Practical Example 5

A nonaqueous solvent having an EC:DMC (ratio by volume) of 1:2 was prepared, and $LiPF_6$ was so dissolved therein to a concentration of 1 M to prepare the electrolytic solution, after which 2.0% by weight of divinyl sulfone (R=vinyl group) were so further added as the additive to the electrolytic solution. Upon manufacturing a coin battery as in Practical Example 1 using this electrolytic solution and measuring the battery characteristics, the initial charge/discharge was nearly equivalent to a case in which only EC-DMC (1/2) was used as the

electrolytic solution (Comparative Example 2), and measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 91.1% when the initial discharge capacity was 100%. In addition, the low-temperature characteristics also were satisfactory. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0031] Practical Example 6

Other than using 2.0% by weight, with respect to the electrolytic solution, of ethylvinyl sulfone (R=vinyl group) and using MEC in place of DMC, the electrolytic solution was prepared and the coin battery was manufactured as in Practical Example 1, and upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 90.4%. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0032] Practical Example 7

Other than using $LiMn_2O_4$ in place of $LiCoO_2$ and using 3.0% by weight, with respect to the electrolytic solution, of divinyl sulfone (R=vinyl group), the electrolytic solution was prepared as in Practical Example 5 and a coin battery was manufactured. Upon measuring the battery characteristics after 50 cycles, the discharge capacity maintenance factor was 89.3%. The manufacturing conditions for the coin battery and the battery characteristics are shown in Table 1.

[0033] Comparative Example 2

A nonaqueous solvent having an EC:DMC (ratio by volume) of 1:2 was prepared and $LiPF_6$ was so dissolved therein to a concentration of 1 M. No additive was added at all at this time. A coin battery was manufactured as in Practical Example 1 using this electrolytic solution and the battery characteristics were measured. The discharge capacity maintenance factor with respect to the initial discharge capacity after 50 cycles was 83.8%. The manufacturing conditions of the coin battery and the battery characteristics are shown in Table 1.

[0034]

[Table 1]

	正極	負極	添加剤	添加量 wt%	電解液組成 (容量比)	50サイクル放電容量維持率%
実施例1	$LiCoO_2$	天然黒鉛	ジビニルスルホン	2.0	1M $LiPF_6$ PC/DMC=1/2	86.1
実施例2	$LiCoO_2$	天然黒鉛	ジビニルスルホン	0.5	1M $LiPF_6$ PC/DMC=1/2	84.7
実施例3	$LiCoO_2$	天然黒鉛	ジビニルスルホン	8.0	1M $LiPF_6$ PC/DMC=1/2	81.1
実施例4	$LiCoO_2$	天然黒鉛	エチルビニルスルホン	2.0	1M $LiPF_6$ PC/DMC=1/2	85.7
比較例1	$LiCoO_2$	天然黒鉛	なし	0.0	1M $LiPF_6$ PC/DMC=1/2	充放電不可
実施例5	$LiCoO_2$	天然黒鉛	ジビニルスルホン	2.0	1M $LiPF_6$ EC/DMC=1/2	91.1
実施例6	$LiCoO_2$	天然黒鉛	エチルビニルスルホン	2.0	1M $LiPF_6$ EC/MEC=1/2	90.4
実施例7	$LiMn_2O_4$	天然黒鉛	ジビニルスルホン	3.0	1M $LiPF_6$ EC/DMC=1/2	89.3
比較例2	$LiCoO_2$	天然黒鉛	なし	0.0	1M $LiPF_6$ EC/DMC=1/2	83.8

Key:

	Positive Electrode	Negative Electrode	Additive	Amount Added (% by weight)	Electrolytic Solution Composition (ratio by volume)	50-Cycle Discharge Capacity Maintenance Factor (%)
Practical Example 1		Natural graphite	Divinyl sulfone			
Practical Example 2		Natural graphite	Divinyl sulfone			
Practical Example 3		Natural graphite	Divinyl sulfone			
Practical Example 4		Natural graphite	Ethylvinyl sulfone			
Comparative Example 1		Natural graphite	None			Charge and discharge are impossible
Practical Example 5		Natural graphite	Divinyl sulfone			
Practical Example 6		Natural graphite	Ethylvinyl sulfone			
Practical Example 7		Natural graphite	Divinyl sulfone			
Comparative Example 2		Natural graphite	None			

[0035] Moreover, the present invention is not limited to the described practical examples, and various combinations readily analogous to the gist of the invention are possible. In particular, the combinations of the solvents of the above-mentioned practical examples are not limited. Furthermore, although the above-mentioned practical examples relate to a coin battery, the present invention can also be applied to a cylindrical or prismatic battery.

[0036]

[Advantages of the Invention] According to the present invention, a lithium secondary battery having outstanding battery

characteristics, such as the battery cycle characteristics, electrical capacity, and storage characteristics, can be provided.